Ceramics Based on Yttrium Aluminum Garnet Containing Nd and Sm Obtained by Spark Plasma Sintering

L.S. Golovkina[1], A.I. Orlova[2], A.V. Nokhrin[3], M.S. Boldin[4], N.V. Sakharov[5]

[1-5]State University of Nizhny Novgorod
603950 Nizhny Novgorod, Russia

[1]golovkina_lyudmila@mail.ru; [2]albina.orlova@gmail.com; [3]nokhrin@nifti.unn.ru; [4]boldin@nifti.unn.ru; [5]metals@nifti.unn.ru

Abstract

Complex oxides containing Nd and Sm with a garnet structure type $Y_{2.5}Nd_{0.5-x}Sm_xAl_5O_{12}$ (x = 0, 0.05, 0.25, 0.45, 0.50) were synthesized by coprecipitation method followed by heating to 1000°C. Ceramic based on $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.50) was prepared by Spark Plasma Sintering method (SPS): $T_{sintering}$=1400°C, $t_{sintering}$=6.5 min. The relative density was 99.6%.

Keywords

Oxides; Garnet Structure; High-Density Ceramic; SPS Method

Introduction

One of the most urgent problems of modern nuclear industry is the development of materials for the immobilization of radioactive wastes for safe storage and, in some cases, for transmutation of minor actinides. For this purpose, in different research centers in the world crystal and ceramic molds of compacting waste are studied. Among them, there are analogues of natural minerals: monazite [*Ewing R.C. et al.*, 1995; *Orlova A.I. at al.*, 2011[2]; *Volkov Yu.F. et al.*, 2002], zircon [*Ewing R.C., 2001*; *Ewing R.C. et al.*, 1995; *Burghatz M. et al.*, 1998; *Lumpkin G.R.*, 2001], garnet [*Burakov B.E. et al.*, 1998, 1999[1], 1999[2], 2000; *Laverov N.P. et al.*, 2010; *Li J.-G. et al.*, 2000; *Suárez M. et al.*, 2009; *Wen L. et al.*, 2004; *Zimina G.V. et al.*, 2010], kosnarit [*Bykov D.M. et al.*, 2006; *Orlova A.I.*, 2002; *Scheetz B.E. et al.*, 1994; *Volkov Yu.F. et al.*, 2002], langbeinite [*Orlova A.I. at al.*, 2011[1], 2011[2]], whitlockite [*Orlova A.I. at al.*, 2006], etc. The structure of garnet is particularly noteworthy for the compaction of f-elements in the oxidation state 3+/4+ (actinides, lanthanides) present in the waste in various combinations and concentrations. Ceramic materials prepared from the compounds with this structure will enhance the "chemical" security barrier to the action of destructive factors of natural and man-made disasters. This, in turn, will ensure the minimization of the risk of radiation exposure on the environment for long-term storage and disposal.

Spark Plasma Sintering (SPS) is an innovative method of producing ceramics which provides for the formation of high-density ceramic product at short time intervals. Short time of sintering is a favorable factor if the work is carried out with radioactive materials, which reduces the release of radioactive components into the environment during the manufacturing process.

Previously, the SPS method was used to prepare composites Nd_2O_3-Nb, modeling Am_2O_3 [*William H.R. et al.*, 2013], the fuel compositions CeO_2 (as analogous to UO_2, PuO_2 Am_2O_3) -W [*O'Brien R.C. et al.*, 2009], UO_2-W [*O'Brien R.C. et al.*, 2013], inert fuels Dy_2O_3 (as simulator Am_2O_3) with ZrC, TiC and ZrN, TiN [*Ryu H.J. et al.*, 2006], the nature of the salt compounds $Ca_{0.5}Zr_2(PO_4)_3$, $NaFeNb(PO_4)_3$ [*Orlova A.I. et al.*, 2012]. Sintering by the SPS method was also used for preparing of $Y_3Al_5O_{12}$ ceramic oxide with garnet structure [*Suárez M. et al.*, 2009]. But this compound didn't contain f-elements.

In the present work, SPS technology has been employed for fabrication ceramics based on complex oxides with garnet structure containing 4f-elements as imitators of minor actinides and lanthanides (products of fission of heavy cores). SPS method had to be used as well as for compounds with garnet structure containing lanthanides for the first time.

Experimental Procedure

Compounds with garnet structure type $Y_{2.5}Nd_{0.5-x}Sm_xAl_5O_{12}$ (x=0, 0.05, 0.25, 0.45, 0.50) were synthesized by coprecipitation method. Aqueous solutions of

reactants ($Al(NO_3)_3 \cdot 9H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$) were mixed with ammonium hydroxide NH_4OH (5% in water) to pH = 8 value. Prepared gel was heated at 90°Cduring the day to remove the water. The dry residue was successively heated at 300°C for 3 h, 500, 800, 1000°C for 20 h at each stage.

Ceramics was obtained by SPS. This method consists in the high heat of the powder material by passing direct current pulses through the sample and the mold with the simultaneous application of hydrostatic pressure.

Sintering was carried out on the installation Dr.Sinter Model-625. The main characteristics of the installation were as follows: a vacuum of up to 5 Pa, gas atmosphere Ar, N_2, the sintering temperature to 2500°C, pressure up to 100 kN, the heating rate to 2500°C/min, the duration of the process to 99 min, current up to 5000 A, the sample diameter ø 10 ÷ 50 mm.

Crystalline graphite powders were placed in a cuvette of 10 mm diameter and heated to 600°C (heating rate 100°C/min), then to 1400°C (heating rate 50°C/min) to 101.9 MPa applied pressure.

The method of differential scanning calorimetry (DSC) was used to determine the formation temperature of the final product. The study was conducted on the installation Setaram LABSYS DSC 1600.

Phase formation was studied by X-ray diffraction analysis (XRD). Recording XRD spectra was carried out on the installation Shimadzu LabX XRD-6000: CuKα-filter, λ = 1.54078Å.

The density of the ceramic was measured by hydrostatic weighing in distilled water at scales Sartorius CPA.

Microcrystallinity of the samples was evaluated by the atomic force microscope Solvet Pro 47 H, equipped with an optical video microscope Optem.

Hydrolytic stability of the obtained ceramics was investigated in a static mode for 28 days at room temperature. For this aim, ceramic was put in a vessel with distilled water (V=20 ml). Sampling of the aqueous solution was performed after 1, 3, 7, 10, 14, 21, 28 days.

The concentration of lanthanide ions was measured by flame atomic absorption spectrometry (AAS) on the instrument Shimadzu AA-7000F (detection limit of Sm^{3+} = 4 mcg/l).

Results and Discussion

The synthesized compounds are polycrystalline powders of different colors and shades, from pale violet for oxide at x = 0 to pale yellow for the oxide at x = 0.5.

Fig. 1 shows the DSC curve for a sample of the precursor oxide $Y_{2.5}Nd_{0.5}Al_5O_{12}$ (x = 0) after heating to 500°C and thermostating for 20 h. In this curve, isothermal peak is present at 925°C that can testify about the course at this temperature solid-state reaction.

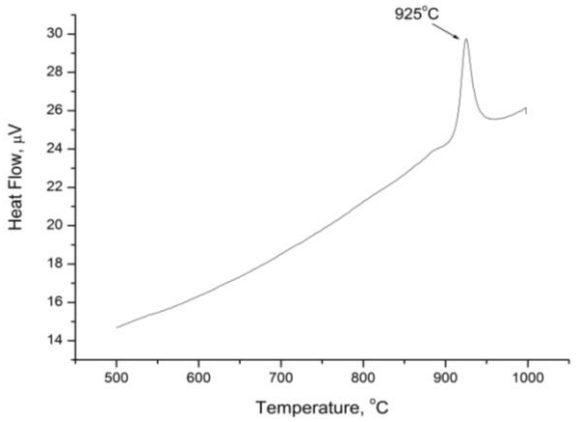

FIG. 1 DSC CURVE FOR AMORPHOUS $Y_{2,5}Nd_{0,5}Al_5O_{12}$ (x = 0)

X-ray data (Fig. 2) are in agreement with the results of DSC. With gradual heating of the reactants and intermediates and thermostating for 20 h at each stage, formation of the final product took place after the heat treatment step at 900°C.

The indexing was done using analog $Y_3Al_5O_{12}$, Sp. Gr. Ia3d [*ICDD Data Base. Card № 79-1891*].

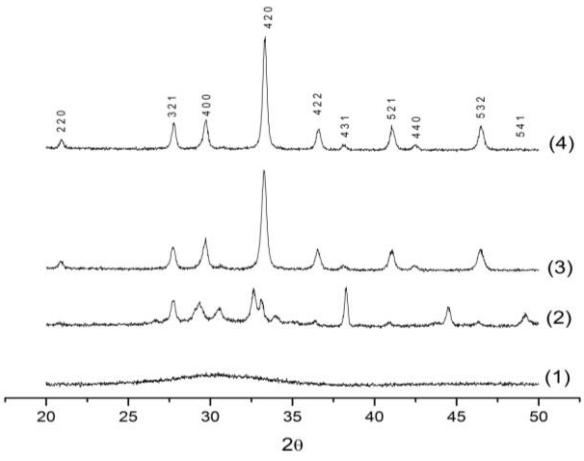

FIG. 2 XRD SPECTRA OF OXIDE $Y_{2,5}Nd_{0,5}Al_5O_{12}$ AFTER HEAT TREATMENT: (1) T = 500°C, (2) T = 800°C, (3) T = 900°C, (4) T = 1000°C.

Taking into account the results of DSC and XRD, other compounds type $Y_{2.5}Nd_{0.5-x}Sm_xAl_5O_{12}$ (x = 0, 0.05, 0.25, 0.45, 0.50) were obtained in thermostating at the final

stage at 1000°C.

Fig. 3 shows XRD spectra of other compounds type $Y_{2.5}Nd_{0.5-x}Sm_xAl_5O_{12}$ (x = 0, 0.05, 0.25, 0.45, 0.50), indicating that when the content of neodymium and samarium is $0 \le x \le 0.5$ in a series of complex oxides $Y_{2.5}Nd_{0.5-x}Sm_xAl_5O_{12}$, the formation of a continuous series of solid solutions takes place. Isostructural phases crystallize in the Sp. Gr. Ia3d [*ICDD Data Base. Card № 79-1891*].

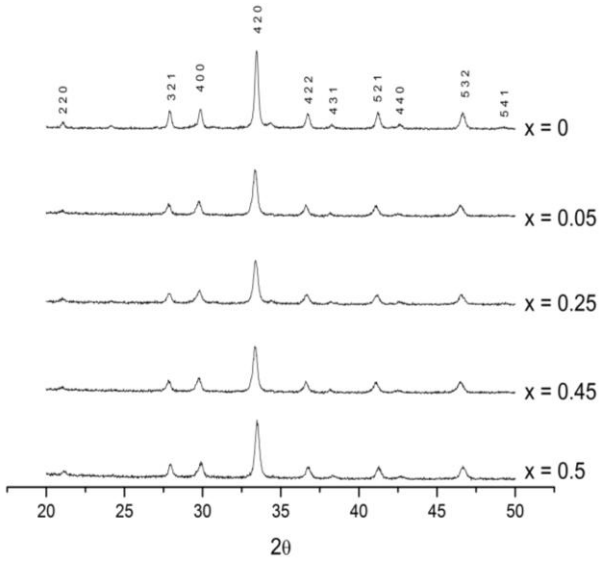

FIG. 3 XRD SPECTRA OF COMPOUNDS TYPE $Y_{2.5}Nd_{0.5-x}Sm_xAl_5O_{12}$ ($0 \le x \le 0.5$)

In the next stage, ceramics have been obtained from prepared powders. Sintering was carried out with an oxide $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.5) using the SPS.

Fig. 4 shows diagrams sintering.

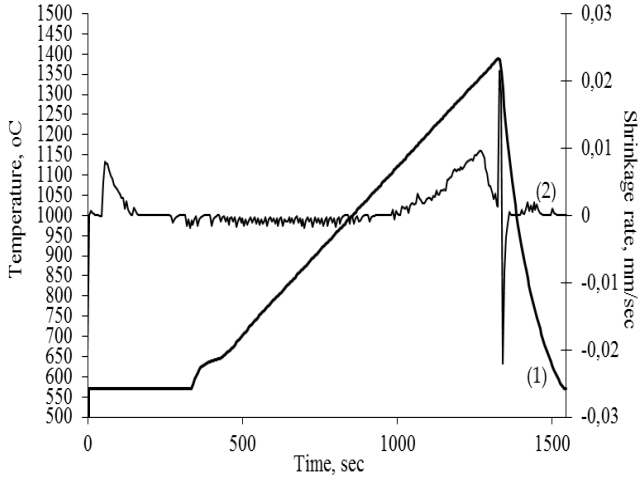

FIG. 4 DIAGRAMS SINTERING OF OXIDE $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.5). CHANGE OF TEMPERATURE WITH TIME (1) AND DEPENDENCE OF THE SHRINKAGE RATE FROM TEMPERATURE (2).

It is evident that shrinkage starts at 1120°C and ends at 1390°C. Its top speed is achieved at 1387°C. Time shrinkage is 6.5 min.

According to the XRD (Fig. 5), the phase composition of the sample was preserved after sintering. The relative intensity of the reflections rose.

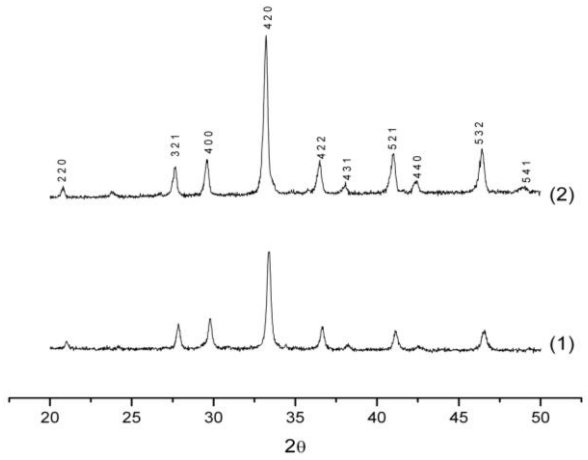

FIG. 5 XRD SPECTRA OF OXIDE $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.5) BEFORE (1) AND AFTER (2) SINTERING.

The relative density of the obtained ceramic was about 99,6% of the theoretical value (4.81 g/cm^3).

The particle size of the ceramic sample was 40-90 nm and agglomerate size didnot exceed 380 nm (Fig. 6).

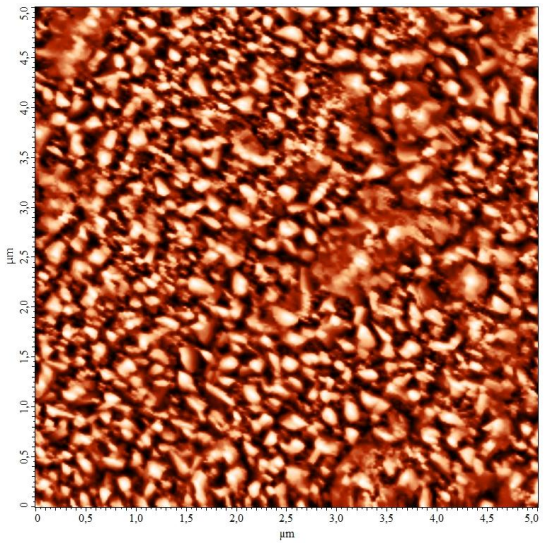

FIG. 6 MICROSTRUCTURE OF THE CERAMIC SAMPLE $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.5).

Hydrolytic stability of the ceramic $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.5, surface area G = 2.51 cm^2) was studied at room temperature for 28 days. The consentrations of samarium in the aqueous samples didn't exceed the limit of detection by flame AAS (<4 mcg/l). The phase composition of the ceramic sample after the experiment has not changed, but intensity of the reflection was reduced (Fig. 7).

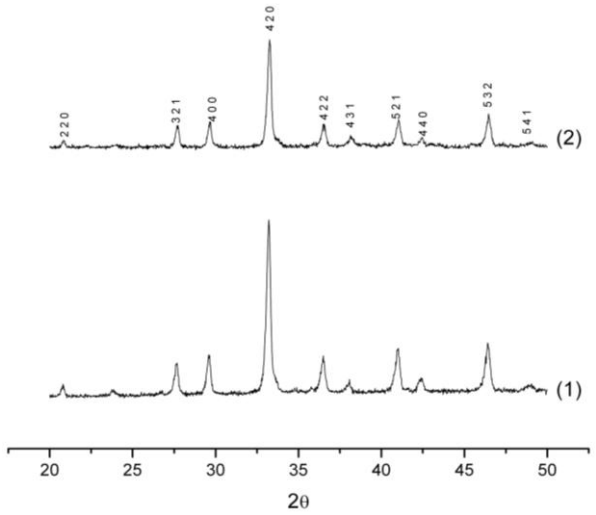

FIG. 7 XRD SPECTRA OF OXIDE $Y_{2.5}Sm_{0.5}Al_5O_{12}$ (x = 0.5) BEFORE (1) AND AFTER (2) LEACHING.

Conclusions

Finally, it is noted that complex oxides with garnet structure containing in its composition the lanthanides can be prepared in the form of dense ceramic (99.6%), using the SPS method. The possibility of forming them for the short time interval (in this paper at the chosen sintering conditions t ≈ 6 min) is practically significant factor, the role of which is particularly significant if a similar process with the compounds of actinides for their compaction to burial or transmutation takes place. High-density ceramic (99%) achieved during the sintering of ceramics by SPS, enhances its chemical stability, in particular hydrolytic, and increases immobilization (chemical) barrier for radioactive material during prolonged storage.

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